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Actinide Structural Studies. 15.* Two 1,10-Phenanthroline Complexes of Uranium(VI)

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Abstract. Dinitratodioxo(1,10-phenanthroline)-uranium(VI) (1): $[UO_2(NO_3)_2(C_{12}H_8N_2)]$, $M_r = 574{\cdot}25$, trigonal, space group $P3_121$, $a = 11{\cdot}303\,(2)$, $c = 10{\cdot}336\,(4)$ Å, $U = 1143{\cdot}5\,(5)$ Å^3, $Z = 3$, $D_m = 2{\cdot}72$, $D_x = 2{\cdot}48$ g cm^{-3}, $F(000) = 792$, $\mu(\text{Mo } K\alpha) = 101{\cdot}22$ cm^{-1}, $T = 290$ K, $R = 0{\cdot}035$ for 1215 unique observed reflections, $[I/\sigma(I) \geq 3{\cdot}0]$. Di-$\mu$-hydroxo-bis[acetatodioxo(1,10-phenanthroline)uranium(VI) (2): $[U_2O_4(OH)_2(C_2H_3O_2)_2(C_{12}H_8N_2)_2]$, $M_r = 1052{\cdot}56$, monoclinic, space group $C2/c$, $a = 23{\cdot}320\,(6)$, $b = 9{\cdot}945\,(4)$, $c = 15{\cdot}978\,(4)$ Å, $\beta = 119{\cdot}14\,(2)°$, $U = 3237\,(2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}16$ g cm^{-3}, $F(000) = 1936$, $\mu(\text{Mo } K\alpha) = 95{\cdot}27$ cm^{-1}, $T = 290$ K, $R = 0{\cdot}060$ for 1994 unique observed reflections. The bond angle of 178·7 (7)° for complex (1) indicates an essentially linear uranyl group. Little information on the corresponding group is available for complex (2) because of severe disorder throughout the structure. Both complexes show steric strain. This is illustrated by the magnitude of the angle between the plane of the phenanthroline ligand and the plane containing the equatorial oxygen atoms and uranium: 18·5 (5) (1) and 12·6 (10)° (2). Such twists are necessary to accommodate the phenanthroline ligand in the equatorial plane.

Introduction. In previous work (Alcock, Flanders & Brown, 1984) we described uranyl complexes with the bidentate *N*-donor ligand 2,2′-bipyridyl. The ability of this ligand to twist about the 1,1′ C—C bond permits it to be accommodated in the equatorial plane of a hexagonal bipyramid. As an extension of this, it was of interest to substitute the more rigid ligand 1,10-phenanthroline, which has similar geometry to bipyridyl, but is constrained by the benzene ring which joins the two pyridyl rings. The synthesis and structures of (1) and (2) are discussed and compared with the 2,2′-bipyridyl analogues.

Table 1. *Crystal data and data collection conditions*

	(1)	(2)
Data collected	$h, \pm k, \pm l$	$h, k, \pm l$
Crystal size (mm)	0·015 × 0·016 × 0·046	0·30 × 0·18 × 0·67
Max. transmission factor	0·44	0·76
Min. transmission factor	0·39	0·23
Scan range about $K\alpha_1$–$K\alpha_2$ (°)	±0·9	±1·1
Reflections collected	3317	2861
Reflections observed $[I/\sigma(I) \geq 3{\cdot}0]$	1215	1994
Weighting constant: g	0·0014	0·0014
R(final)	0·035	0·060
wR(final)	0·039	0·065
Max. $\Delta\rho$ on final ΔF map (e Å^{-3})	1·1	2·0
Min. $\Delta\rho$ on final ΔF map (e Å^{-3})	−1·0	−1·9
Max. Δ/σ (final cycle)	0·094	0·18

Experimental. Both compounds were prepared by the technique of liquid diffusion. For (1) a saturated ethanolic solution (2 cm^3) of 1,10-phenanthroline was layered on top of a saturated solution of uranyl nitrate (2 cm^3). Compound (2) was prepared in an analogous way, layering a saturated uranyl acetate solution on top of the solution of 1,10-phenanthroline. In each case, the tubes were carefully sealed. When the two solutions had completely mixed, the crystals which had formed at the interface were filtered off and washed with ice-cold ethanol. The product with uranyl acetate was found to be an (OH)-bridged dimer from the structure determination.

Data were collected with a Syntex $P2_1$ automatic four-circle diffractometer for 2θ in the range 3–50°. Background intensities were measured at each end of the scan for 0·25 of the scan time. Three standard reflections, monitored every 200 reflections, showed slight changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22°$). Observed reflections $[I/\sigma(I) \geq 3{\cdot}0]$ were corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970). Details for each compound are given in Table 1.

Heavy atoms were located by Patterson methods, and the remaining lighter atoms by successive Fourier syntheses. For (1), systematic absences $000l$: $l \neq 3n$ indicated space group $P3_121$ and the U atom was found at special position $3(a)$ $(x, 0, \frac{1}{3})$, with the molecule lying

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* Part 14: Alcock & Flanders (1987).

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on a twofold axis. Systematic absences for (2), *hkl*: $h + k \neq 2n$ and *h*0*l*: $l \neq 2n$ indicated a choice of two possible space groups: *C*2/*c* and *Cc*. Structure solution in *C*2/*c* located the phenanthroline ligand (and acetate group) and indicated that the molecule was a centrosymmetric dimer. However, maps showed two bridging atoms implausibly close to each other; the uranyl O positions were also duplicated. Refinement was continued with both sets of positions included at half occupancy. During final refinement, a smaller bridging O peak was also located, and the bridging atom is represented by O(51), O(52) and O(53) with occupancies 0·4, 0·4 and 0·2 respectively. A group of residual peaks distant from the main complex was interpreted as a partially occupied disordered solvent molecule [C(001)—C(004), with occupancies 0·5, 0·5, 0·25, 0·25].

All of the relatively large residuals on the final difference maps lay close to the U atoms. The true structure is presumably a non-centrosymmetric dimer with one set of uranyl O atoms on each U; this gives reasonable O(axial)—U—O(equatorial) angles. An attempt to refine this structure in space group *Cc* was, however, unsuccessful, either because of the high correlations between pseudo-related atoms or because the actual crystal studied was made up of molecules in both orientations.

Anisotropic temperature factors were used for all atoms except the hydrogens [complex (1)] and for the ordered atoms in complex (2). In each complex H atoms were inserted at fixed positions ($U = 0{\cdot}07$ Å^2). Hydroxo H atoms in (2) were not included. Final refinement on *F* was by cascaded least-squares methods. A weighting scheme of the form $w = 1/[\sigma^2(F) + g(F^2)]$ was applied. Calculations for (1) were carried out on a Data General NOVA3 minicomputer using the *SHELXTL* system (Sheldrick, 1981), those for (2) used a Data General DG30 in addition to the NOVA3. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 2, and significant bond lengths and angles in Table 3. Table 4 contains details of the least-squares planes.*

Table 2. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}
(1)				
U(1)	4323·3 (5)	0	3333	49 (1)
O(1)	4572 (10)	533 (10)	4934 (10)	70 (4)
O(2)	5610 (12)	−1255 (12)	3568 (13)	93 (6)
O(3)	3566 (12)	−2306 (11)	4256 (12)	93 (6)
O(4)	4818 (18)	−3257 (15)	4435 (17)	140 (9)
N(1)	4646 (17)	−2327 (15)	4156 (16)	92 (8)
N(2)	3076 (16)	1363 (16)	3283 (10)	68 (6)
C(1)	3772 (29)	2729 (24)	3310 (14)	97 (14)
C(2)	3062 (37)	3474 (30)	3356 (17)	141 (22)
C(3)	1696 (39)	2827 (37)	3343 (16)	170 (30)
C(4)	953 (28)	1413 (34)	3347 (14)	130 (22)
C(5)	1672 (24)	700 (23)	3295 (15)	95 (14)
C(6)	−506 (31)	655 (45)	3318 (34)	194 (47)
(2)				
U(1)	3477·1 (3)	8128·1 (6)	5367·0 (5)	64 (1)
O(11)*	4026 (9)	6899 (17)	6411 (14)	53 (5)
O(21)*	2992 (15)	9085 (27)	4461 (19)	91 (8)
O(12)*	3616 (12)	6846 (20)	6018 (17)	67 (6)
O(22)*	3307 (12)	9562 (23)	4478 (17)	76 (6)
O(3)	4273 (6)	9850 (13)	6381 (10)	94 (8)
O(4)	3420 (7)	9658 (14)	6542 (11)	108 (9)
O(51)†	2352 (12)	8558 (22)	4933 (18)	48 (5)
O(52)†	2623 (11)	7393 (27)	5732 (17)	49 (6)
O(53)†	2464 (25)	6993 (53)	4592 (41)	51 (12)
N(1)	4556 (6)	7849 (12)	5249 (10)	66 (7)
N(2)	3442 (7)	6525 (13)	4059 (10)	61 (6)
C(1)	5122 (10)	8463 (22)	5885 (17)	102 (13)
C(2)	5727 (10)	8276 (23)	5897 (18)	105 (13)
C(3)	5768 (10)	7400 (24)	5286 (17)	104 (13)
C(4)	5166 (9)	6699 (16)	4573 (13)	70 (9)
C(5)	5130 (11)	5749 (19)	3872 (15)	90 (13)
C(6)	4590 (10)	5132 (20)	3306 (15)	82 (11)
C(7)	3987 (9)	5395 (17)	3306 (12)	71 (9)
C(8)	3411 (10)	4764 (18)	2701 (13)	91 (12)
C(9)	2830 (12)	5026 (26)	2718 (14)	108 (12)
C(10)	2932 (11)	5904 (20)	3472 (14)	95 (13)
C(11)	3988 (7)	6268 (15)	3987 (9)	53 (7)
C(12)	4561 (8)	6965 (13)	4615 (11)	58 (8)
C(13)	3936 (9)	10258 (17)	6751 (12)	70 (9)
C(14)	4132 (11)	11391 (22)	7426 (18)	115 (13)
C(001)‡	2081 (38)	1426 (75)	4939 (56)	146 (26)
C(002)‡	2429 (41)	2593 (83)	5455 (56)	153 (23)
C(003)‡	2239 (50)	2124 (92)	4733 (79)	89 (24)
C(004)‡	1876 (39)	1378 (79)	4440 (60)	71 (19)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

* Occupancies O(11)–O(22) 0·5.

† Occupancies O(51), O(52) 0·4; O(53) 0·2.

‡ Occupancies C(001), C(002) 0·5; C(003), C(004) 0·25.

Discussion. Both complexes exhibit distorted hexagonal-bipyramidal geometry about the central uranyl group which is coordinated to four O and two N atoms in the equatorial plane, and thus they are similar to the complexes with 2,2′-bipyridyl which has the same bite distance [mean N···N of 2·67 (2) Å in the four complexes previously described].

In (1) (Fig. 1), the U—O(UO_2^{2+}) bond length [1·735 (10) Å] is shorter than the average value [1·78 (3) Å] found in other hexagonal-bipyramidal uranyl complexes (Denning, 1983). The U—N(ligand) bond length [2·557 (22) Å] is similar to those previously reported (Bandoli, Clemente, Maragoni & Paolucci, 1978, 1980) and not significantly shorter than the values found in the 2,2′-bipyridyl complexes. U—O(NO_3) bond lengths [2·490 (12) and 2·500 (17) Å] are as expected from other uranyl nitrate

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* Lists of structure factors and anisotropic thermal parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44504 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and angles* (°) *about the uranium atom with e.s.d.'s in parentheses* (*primed atoms are related to unprimed by a twofold axis*)

(1)

U–O(1)	1·735 (10)	U–O(3)	2·491 (12)
U–O(2)	2·500 (17)	U–N(2)	2·556 (22)
O(1)–U–O(1)′	178·7 (7)	O(2)–U–O(3)′	109·1 (4)
O(1)–U–O(2)	93·7 (5)	O(2)–U–N(2)′	118·7 (5)
O(1)–U–O(2)′	87·4 (5)	O(3)–U–N(2)	129·3 (4)
O(1)–U–O(3)	84·8 (4)	O(3)–U–O(2)′	109·1 (5)
O(1)–U–O(3)′	95·4 (4)	O(3)–U–O(3)′	159·3 (6)
O(1)–U–N(2)	81·5 (5)	O(3)–U–N(2)′	70·9 (5)
O(1)–U–N(2)′	97·3 (4)	N(2)–U–O(2)′	118·7 (5)
O(2)–U–O(3)	50·4 (4)	N(2)–U–O(3)′	70·9 (5)
O(2)–U–N(2)	175·2 (4)	N(2)–U–N(2)′	63·0 (7)
O(2)–U–O(2)′	60·1 (6)		

(2)

U(1)–O(1)	1·94 (3)	U(1)–O(5)	2·34 (5)
U(1)–O(2)	1·62 (4)	U(1)–O(6)	2·41 (4)
U(1)–O(3)	2·50 (2)	U(1)–N(1)	2·65 (3)
U(1)–O(4)	2·46 (3)	U(1)–N(2)	2·63 (2)
O(1)–U(1)–O(2)	168·3 (24)	O(1)–U(1)–N(2)	93·7 (12)
O(1)–U(1)–O(3)	85·8 (9)	O(2)–U(1)–N(1)	86·1 (15)
O(2)–U(1)–O(3)	103·4 (17)	O(2)–U(1)–N(2)	86·2 (13)
O(1)–U(1)–O(4)	89·4 (13)	O(3)–U(1)–N(1)	70·5 (8)
O(2)–U(1)–O(4)	90·5 (21)	O(3)–U(1)–N(2)	133·0 (8)
O(1)–U(1)–O(5)	116·1 (7)	O(4)–U(1)–N(1)	122·4 (7)
O(2)–U(1)–O(5)	53·4 (26)	O(4)–U(1)–N(2)	173·7 (7)
O(1)–U(1)–O(6)	81·9 (15)	O(3)–U(1)–O(4)	52·6 (9)
O(2)–U(1)–O(6)	87·1 (25)	O(5)–U(1)–O(6)	34·5 (12)
O(1)–U(1)–N(1)	77·1 (15)	N(1)–U(1)–N(2)	63·8 (7)

Table 4. *Deviations* (Å) *from mean planes* (*primed atoms are related to unprimed by a twofold axis; starred atoms define planes; e.s.d.'s* ±0·05 Å)

(1)
Plane 1
U* 0·00; O(2)* –0·13; O(3)* 0·25; N(2)* 0·34; O(2)′* 0·13; O(3)′* –0·25; N(2)′* –0·34
Plane 2
N(2)* –0·03; C(1)* 0·02; C(5)* –0·01; C(5)′* 0·01; C(1)′* –0·02; N(2)′* 0·03
Plane 3
O(2)* –0·01; O(3)* –0·01; O(4)* –0·01; N(1)* 0·03
Line 4
O(1)*; O(2)*

Angles between plane normals and line (°) (e.s.d. 0·5°)

1:2	16·2
1:3	10·7
1:4	0·4
2:3	25·4
2:4	16·6
3:4	10·4

(2)
Plane 1
U(1)* –0·01; O(3)* 0·02; O(4)* 0·02; C(13)* –0·03
Plane 2
N(1)* –0·03; N(2)* 0·01; C(1)* 0·02; C(10)* 0·00; C(11)* 0·01; C(12)* –0·01
Plane 3
O(3)* 0·02; O(4)* 0·02; C(13)* –0·01; C(14)* 0·00
Line 4
O(11)*; O(21)*

Angles between plane normals and line (°) (e.s.d. 1·0°)

1:2	14·5
1:3	3·4
1:4	7·6
2:3	16·2
2:4	21·1
3:4	6·5

compounds (Cattalini, Croatto, Degetto & Tondello, 1971; Barclay, Sabine & Taylor, 1965), but compression is apparent in the O···O distance between the two nitrate groups [2·51 (2) Å] which is considerably less than the expected 2·7–2·8 Å. A consequence of this is seen in the O···N distance between the nitrate group and the phenanthroline ligand. This ligand is pivoted as a unit about the line from U to the centre of the 5,5′ C—C bond, producing a relatively long O···N interligand contact distance of 2·93 (4) Å. The nitrate anions are also rotated so that O(2) and O(2′) are twisted 0·04 (5) Å alternately above and below the mean equatorial plane [defined by U—O(2)—O(3)—N(2)—O(2′)—O(3′)—N(2′)] whilst O(3), O(3′) lie in this plane. The angle between the plane of the phenanthroline and the mean equatorial plane of the complex [25·4 (6)°] is only slightly larger than that observed in the 2,2′-bipyridyl compound [22·0 (4)°]. Fig. 2 shows this twist clearly and reveals that the overall packing of (1) is controlled by a face-to-face interaction of the phenanthroline ligand.

Fig. 3 shows an idealized view of (2), in which one pair of uranyl O atoms is associated with each U atom, and in which only one set of bridging OH groups is included. Detailed discussion of the dimensions is hampered by the disorder which leads to abnormal values for U—O(uranyl), whose apparent range is 1·57 (2)–1·96 (2) Å. However, the U—N and U—O-(equatorial) seem to be less affected. The U—O-(bridging) and (acetate) have normal values [range

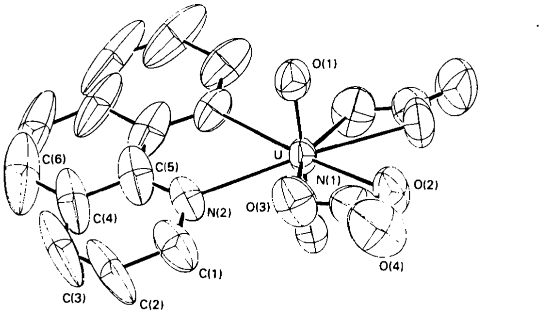
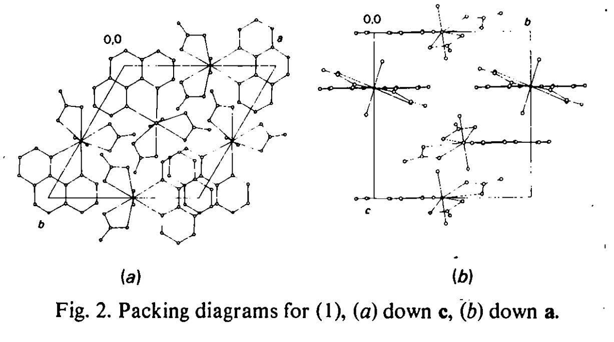


Fig. 1. View of (1), showing the atomic numbering (H atoms omitted).



(*a*) (*b*)

Fig. 2. Packing diagrams for (1), (*a*) down **c**, (*b*) down **a**.

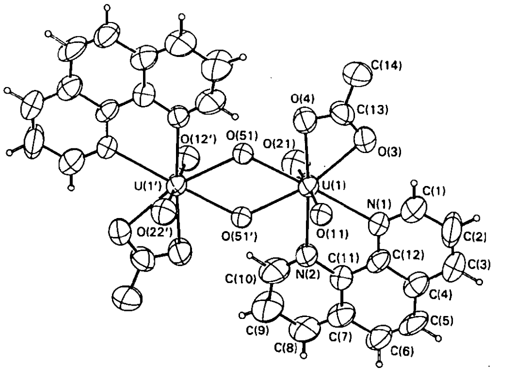


Fig. 3. View of (2), as an idealized non-centrosymmetric dimer, with O(11) and O(21) associated with U(1), and O(12) and O(22) [as the centrosymmetrically-related equivalents O(12′) and O(22′)] associated with U(1′); only O(51) and O(51′) are included as bridging hydroxide positions.

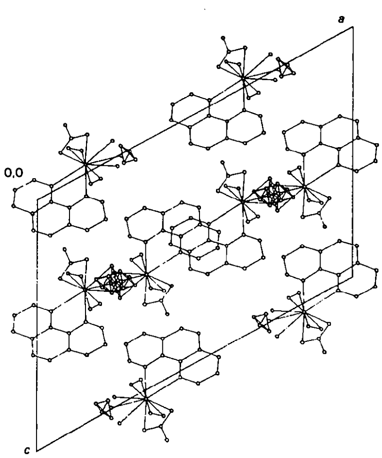


Fig. 4. Packing diagram for (2), viewed down **b**. The alternative positions for the uranyl and bridging oxygen atoms can be seen.

2·34 (5)–2·42 (4) and 2·46 (1)–2·47 (2) Å]. Again these are similar to values previously observed (Alcock, Flanders & Brown 1984), but there is a possible lengthening of the U—N(ligand) bonds to 2·65 (3) and 2·63 (2) Å compared with 2·56 (2) Å found in (1). The O···N (acetate–phenanthroline) contact [2·97 (2) Å] is slightly longer than the equivalent distance found in the 2,2′-bipyridyl complex [2·96 (1) Å]. This may be caused by the need to accommodate the more rigid ligand in the equatorial plane, but it should also be borne in mind that one complex has two nitrate ligands and the other has one acetate and two hydroxides. The atoms which form the equatorial plane are again puckered with deviations in the range −0·18 (5) to 0·15 (5) Å. The coordinating ligands are substantially displaced out of the equatorial plane [by up to 0·61 (5) Å] as seen in Table 4. The acetate group is displaced slightly out of the equatorial plane with a bite [2·20 (1) Å] similar to that found in the 2,2′-bipyridyl analogue [2·16 (1) and 2·17 (1) Å]. The packing diagram, Fig. 4, again indicates a face-to-face alignment of the aromatic rings.

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References

Alcock, N. W. (1970). In *Crystallographic Computing*, edited by F. R. Ahmed, pp. 271–278. Copenhagen: Munksgaard.

Alcock, N. W. & Flanders, D. J. (1987). *Acta Cryst.* C**43**, 1480–1483.

Alcock, N. W., Flanders, D. J. & Brown, D. (1984). *Inorg. Chim. Acta*, **94**, 279–282.

Bandoli, G., Clemente, D. A., Maragoni, G. & Paolucci, G. (1978). *J. Chem. Soc. Chem. Commun.* pp. 235–236.

Bandoli, G., Clemente, D. A., Maragoni, G. & Paolucci, G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1304–1311.

Barclay, G. A., Sabine, T. M. & Taylor, J. C. (1965). *Acta Cryst.* **19**, 205–209.

Cattalini, L., Croatto, U., Degetto, S. & Tondello, E., (1971). *Inorg. Chim. Acta Rev.* **5**, 19–43.

Denning, R. G. (1983). *Properties of the* UO_2^{n+} (n = 1,2) *Ions*. In *Gmelin Handbuch, URAN Suppl. Vol.* A6, pp. 31–79.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Sheldrick, G. M. (1981). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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Polymeric Bis(*O*-methyldithiocarbonato)lead(II)

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Abstract. $[Pb(S_2COCH_3)_2]$, $M_r = 421{\cdot}5$, monoclinic, $C2$, $a = 12{\cdot}285\,(5)$, $b = 4{\cdot}2596\,(7)$, $c = 10{\cdot}060\,(3)$ Å, $\beta = 108{\cdot}04\,(3)°$, $V = 500\,(2)$ Å^3, $D_x = 2{\cdot}800$ Mg m^{-3} for $Z = 2$, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 17{\cdot}693$ mm^{-1}, $F(000) = 384$, $T = 295\,(2)$ K, $R = 0{\cdot}058$ for 455 observed reflections. The Pb atom in $Pb(S_2COCH_3)_2$ is

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